

WHAT IS CLAIMED IS:

1. A process for the production of a liquid hydrocarbon oil, comprising the steps of:

5 (a) mixing a gas feed, containing a lower hydrocarbon having 1-4 carbon atoms and 10-50 mole % of CO<sub>2</sub> based on a total mole of the CO<sub>2</sub> and the lower hydrocarbon, with H<sub>2</sub>O to obtain a mixed gas having contents of the CO<sub>2</sub>, H<sub>2</sub>O and lower hydrocarbon satisfying 10 the following condition:

$$0.5 \leq ([CO_2] + [H_2O])/[C] \leq 2.5$$

wherein [CO<sub>2</sub>] represents the moles of the CO<sub>2</sub>, [H<sub>2</sub>O] represents the moles of the H<sub>2</sub>O and [C] represents the moles of carbon of the lower hydrocarbon;

15 (b) contacting said mixed gas with a catalyst at a temperature of 600-1,000°C and a pressure of 10-75 atm to produce a synthesis gas with a carbon conversion efficiency Cf of at least 50 % and a synthesis gas production efficiency Yf of at least 80 %,

20 said synthesis gas production efficiency Yf being represented by the following formula:

$$Yf = \{[CO] + [H_2]\}/([C] + [CO_2] + [H_2O]) \times 100 \%$$

wherein [CO] represents the moles of CO in said synthesis gas, [H<sub>2</sub>] represents the moles of H<sub>2</sub> in said synthesis gas, 25 and [CO<sub>2</sub>], [H<sub>2</sub>O] and [C] are as defined previously,

said carbon conversion efficiency Cf being represented by the following formula:

$$Cf = {[CO]}/([C] + [CO_2]) \times 100 \%$$

wherein [CO], [CO<sub>2</sub>] and [C] are as defined previously,

30 said synthesis gas having a molar ratio of hydrogen to carbon monoxide of 1.5-2.5,

said catalyst having a specific surface area of 5 m<sup>2</sup>/g or less and comprising a magnesium oxide-containing carrier and at least one catalytic metal selected from the 35 group consisting of rhodium and ruthenium and supported on

said carrier in an amount of 10-5,000 ppm, in terms of elemental metal, based on the weight of said carrier;

(c) reacting said synthesis gas in the presence of a Fischer-Tropsch catalyst having a low CO shift reaction activity to obtain a product containing a liquid hydrocarbon oil; and

(d) separating said liquid hydrocarbon oil from said product.

10 2. A process as claimed in claim 1, wherein said gas feed contains 20-40 mole % of CO<sub>2</sub> and wherein said mixed gas satisfies the following condition:

$$1 \leq ([\text{CO}_2] + [\text{H}_2\text{O}])/[\text{C}] \leq 2$$

wherein [CO<sub>2</sub>], [H<sub>2</sub>O] and [C] are as defined in claim 1.

15 3. A process as claimed in claim 1, wherein said gas feed is discharged overhead from a distillation tower where a raw material feed containing CO<sub>2</sub> and a lower hydrocarbon is distilled at a pressure of 10-80 atm while 20 removing CO<sub>2</sub> from a bottom thereof.

4. A process as claimed in claim 3, wherein said distillation tower is operated at a pressure of 20-50 atm and a tower top temperature of -60°C.

25 5. A process as claimed in claim 1, wherein said Fischer-Tropsch catalyst comprises Co and/or Ru as catalytic metal thereof.

30 6. A process as claimed in claim 1, further comprising subjecting said liquid hydrocarbon oil separated in step (d) to catalytic hydrogenation and/or catalytic hydrocracking to obtain gasoline, kerosene and gas oil.

35 7. A process as claimed in claim 1, further comprising

separating a gas product containing methane, hydrogen and carbon dioxide from said product in step (d), and using at least part of said gas product as a heat energy source in step (b).

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8. A process as claimed in claim 1, further comprising separating a light hydrocarbon fraction containing olefins from said product in step (d), and recycling at least part of said light hydrocarbon fraction to step (c).

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9. A process for the production of dimethyl ether, comprising the steps of:

15 (a) mixing a gas feed, containing a lower hydrocarbon having 1-4 carbon atoms and 30-70 mole % of CO<sub>2</sub> based on a total mole of the CO<sub>2</sub> and the lower hydrocarbon, with H<sub>2</sub>O to obtain a mixed gas having contents of the CO<sub>2</sub>, H<sub>2</sub>O and lower hydrocarbon satisfying the following condition:

$$0.5 \leq ([CO_2] + [H_2O])/[C] \leq 2.5$$

20 wherein [CO<sub>2</sub>] represents the moles of the CO<sub>2</sub>, [H<sub>2</sub>O] represents the moles of the H<sub>2</sub>O and [C] represents the moles of carbon of the lower hydrocarbon;

25 (b) contacting said mixed gas with a catalyst at a temperature of 600-1,000°C and a pressure of 10-75 atm to produce a synthesis gas with a synthesis gas production efficiency Yf of at least 80 % and a carbon conversion efficiency Cf of at least 50 %,

30 said synthesis gas production efficiency Yf being represented by the following formula:

Yf = {[CO] + [H<sub>2</sub>]}/{[C] + [CO<sub>2</sub>] + [H<sub>2</sub>O]}) x 100 %  
wherein [CO] represents the moles of CO in said synthesis gas, [H<sub>2</sub>] represents the moles of H<sub>2</sub> in said synthesis gas, and [CO<sub>2</sub>], [H<sub>2</sub>O] and [C] are as defined previously,

35 said carbon conversion efficiency Cf being represented by the following formula:

$$C_f = \{[CO]/([C] + [CO_2])\} \times 100 \%$$

wherein [CO], [CO<sub>2</sub>] and [C] are as defined previously,  
said synthesis gas having a molar ratio of hydrogen  
to carbon monoxide of 0.5-1.5,

5        said catalyst having a specific surface area of 5  
m<sup>2</sup>/g or less and comprising a magnesium oxide-containing  
carrier and at least one catalytic metal selected from the  
group consisting of rhodium and ruthenium and supported on  
said carrier in an amount of 10-5,000 ppm, in terms of  
10      elemental metal, based on the weight of said carrier;

      (c) reacting said synthesis gas in the presence of  
one or more catalysts having activities of methanol  
synthesis, methanol dehydration and CO shift reaction to  
obtain a product containing dimethyl ether; and

15      (d) separating said dimethyl ether from said product.

10. A process as claimed in claim 9, wherein said gas  
feed contains 40-60 mole % of CO<sub>2</sub> and wherein said mixed  
gas satisfies the following condition:

20       $1 \leq ([CO_2] + [H_2O])/[C] \leq 2$

wherein [CO<sub>2</sub>], [H<sub>2</sub>O] and [C] are as defined in claim 9.

11. A process as claimed in claim 9, wherein said gas  
feed is discharged overhead from a distillation tower  
25      where a raw material feed containing CO<sub>2</sub> and a lower  
hydrocarbon is distilled at a pressure of 10-80 atm while  
removing CO<sub>2</sub> from a bottom thereof.

12. A process as claimed in claim 11, wherein said  
30      distillation tower is operated at a pressure of 20-50 atm  
and a tower top temperature of -60°C.

13. A process as claimed in claim 9, wherein step (c) is  
performed using at least two catalysts selected from the  
35      group consisting of a methanol synthesis catalyst, a

methanol dehydration catalyst and a CO shift reaction catalyst.